

Catalytic combustion of aromatic solvents over Pt catalysts. Steady-state and dynamic behaviour

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STEADY-STATE AND DYNAMIC BEHAVIOUR

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## CATALYTIC COMBUSTION OF AROMATIC SOLVENTS OVER Pt CATALYSTS. STEADY-STATE AND DYNAMIC BEHAVIOUR

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### Introduction

Deep catalytic oxidation of gas emissions containing Volatile Organic Compounds (VOC) is a widely employed technology for air pollution control. Noble metal catalysts are widely employed for their high activity, while monolithic supports offer the best performances as a consequence of their high surface-area to catalyst-volume ratio and low pressure drop (Barresi *et al.*, 1989).

In traditional applications catalytic incineration is usually carried out in the mass transfer controlled regime; thus very little work has been done to elucidate the reaction mechanism for complete oxidation of VOCs.

Actually some problems can arise in practical applications:

- mixtures of VOCs must be handled. Significant "mixture effects" can occur, that cannot be predicted *a priori* unless the true reaction mechanism is known (Spivey, 1987; Barresi, 1990; Barresi and Baldi, 1994): as a consequence the ignition temperature of the combustor can increase, or its Destruction and Removal Efficiency (DRE) can be affected, as the destructibility scale of the compounds, obtained from tests in which the VOCs are alone, may significantly change in the mixture.
- it may be necessary to treat very lean emissions, or to design "zero-emission devices", that is apparatuses that give extra low outlet pollutant concentrations. In this case a microkinetic analysis approach may be necessary, and it must be considered that in these conditions the approximate rate equations obtained at higher concentrations may not be valid; in fact, they are based on transition state theory that assumes Maxwell-Boltzmann equilibrium among reacting molecules and the quasi steady-state approximation (Boudart, 1994; Dumesic *et al.*, 1993).
- non-stationary conditions must be considered. These are important not only during the start up or the transient behaviour of the afterburner designed to operate in steady state; in order to handle very lean mixtures avoiding the need for expensive heating to reaction temperature, periodic operations can be adopted, reversing periodically the flow direction (Matros, 1985; Eigenberger and Nieken, 1994). Kinetic models developed under steady state conditions are *a priori* not suitable to predict the dynamic behaviour, as the model parameters determined under stationary conditions are in general lumped (Renken *et al.*, 1989; Renken, 1993). Of course this is particularly true for complex mixtures, because the dynamics of the different species must be taken into account: mixture effects may greatly affect the periodic behaviour of a combustor.

It is therefore apparent the necessity to have reliable kinetic models able to describe both the steady state and the dynamic behaviour of the reactor. To this purpose the true kinetic mechanism must be understood, and the individual reaction steps must be modelled; steady state experiments are generally not sufficient to validate a dynamic model, and the transient behaviour must be investigated.

In this work steady state and dynamic kinetic data for the deep oxidation of aromatic solvents at low and very low concentrations are presented. The behaviour of both single compounds and multicomponent mixtures has been investigated; mixture effects in the kinetics and in the mass

transfer controlled regime are discussed. The kinetic model previously proposed by the authors has been modified to account for the transient behaviour.

## Experimental set up

The apparatus used in previous works (Barresi and Baldi, 1992; 1994) has been slightly modified to allow dynamic experiments.

The air is filtered and pass through a molecular sieve bed to eliminate CO<sub>2</sub> and water. The liquid VOC is added by means of a metering pump. The mixture is electrically preheated and then converted in an insulated tubular reactor containing a Pt based monolithic catalyst supplied by Engelhard.

The temperature is measured before and after the catalytic bed using two type-K thermocouples.

Inlet and outlet hydrocarbon concentration is measured by gaschromatography; the outlet CO<sub>2</sub> and CO concentration is continuously monitored using a on-line NDIR spectrophotometer (with a 1 s time constant).

Steady state conversion rates have been determined for benzene, toluene, ethylbenzene, *o*-xylene and ethenylbenzene (styrene), and for their mixtures (containing up to four compounds). Concentrations lower than 2000 ppmV have been investigated.

The dynamic response to a reverse step in VOC concentration has been investigated measuring the outlet CO and CO<sub>2</sub> concentration continuously; a four-way valve has been added to the plant that allows to bypass the VOC feeding section stopping the reactant input without disturbing significantly the flow. Single compounds and binary mixtures have been studied. Experiments are in progress and tests in which the oxygen flow is stopped have also been planned.

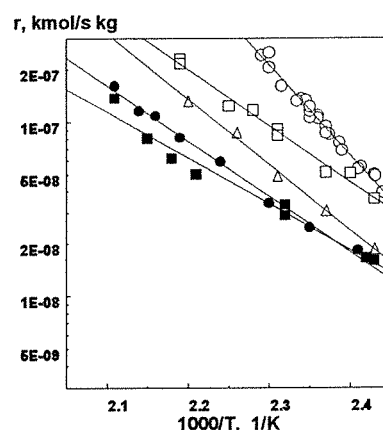


Fig. 1 - Conversion rates of the different aromatics oxidised alone; concentration in the range 500-2000 ppmV, in air. O, benzene; □, toluene; Δ, ethylbenzene; ●, *o*-xylene; ■, styrene.

## Results and discussion

### Steady state single compound oxidation rate

Previous results have evidenced that all the tested aromatic compounds show an apparent zeroth reaction order with respect to the hydrocarbon over a relatively wide concentration range; as concerns the dependence on oxygen concentration, on the contrary, an apparent first order is observed for benzene, while a lower fractional order is shown by the other aromatics (Mazzarino and Barresi, 1993; Barresi and Baldi, 1994). Only CO<sub>2</sub> and water are formed as oxidation products: neither CO nor partial oxidation compounds have been observed.

The conversion rates of the different hydrocarbons in air, in the range where they are independent of the hydrocarbon concentration, are compared in Figure 1. It can be observed that the conversion rate decreases in the order: benzene > toluene > ethylbenzene > *o*-xylene > styrene.

At very low concentration a negative reaction order with respect the hydrocarbon can be evidenced: toluene is shown as an example in Figure 2. This behaviour is indicative of auto-inhibition and saturation effects, as a consequence of strong adsorption on the catalyst. The VOC partial pressure at which saturation is reached is dependent on the reaction temperature, as expected.

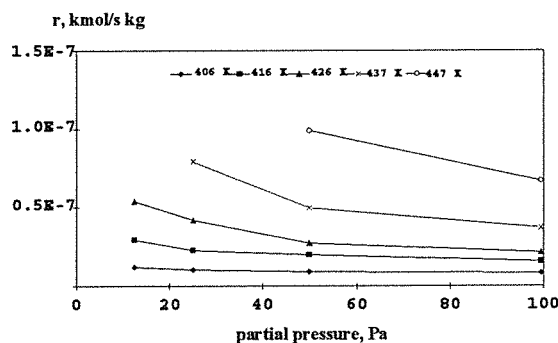


Fig. 2 - Toluene conversion rate in air, as a function of hydrocarbon partial pressure.

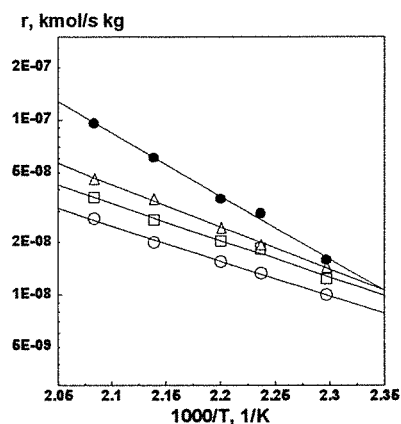


Fig. 3 - Conversion rate of the individual species in a four-compound mixture; about 500 ppmV of each component, in air. ○, benzene; □, toluene; Δ, ethylbenzene; ●, o-xylene.

strength of adsorption of the other competing species (Barresi and Baldi, 1994).

Kinetic inhibition effects cause rising the reactor ignition temperature. It has been shown that in binary mixtures significant increases can be observed in presence of very low styrene concentrations (Barresi *et al.*, 1992). In Figure 4 the conversion curves determined in the pilot plant for a four-component mixture are shown as an example: the curves obtained for the pure benzene (at different inlet concentrations) are shown for comparison.

The behaviour in the diffusion control regime has been also investigated (inlet temperature in the range 250-350°C). At high temperature the conversion should not be affected by kinetic mixture effects, but the results of the experiments are confused: for benzene, for example, an increase of conversion is observed in the mixtures, at constant preheating temperature. If the composition of the mixture changes, the heat of combustion changes too, and differences in the reactor temperature profile cause differences in the diffusion coefficient and therefore in the final conversion.

To highlight this point the relationship between driving force and total conversion has been analysed. In Figure 5 the data for pure benzene and benzene-containing mixtures are shown as an example;  $J_0$  is the product of the diffusivity (evaluated at the average temperature in the reactor) and the inlet concentration, and is

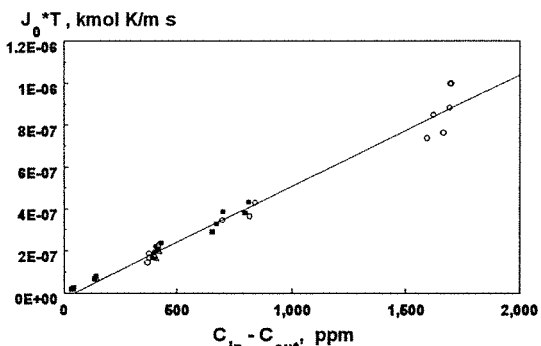


Fig. 5 - Conversion in the diffusion control regime of benzene: pure (○) and in binary mixture with toluene (□), ethylbenzene (Δ), o-xylene (●), styrene (■).

In air; space velocity = 134,000 h<sup>-1</sup>.

### Mixture inhibition effects

Strong inhibition effects are observed when the compounds are not oxidised alone; generally, the conversion rate of all the compounds is reduced, but not in the same proportion.

If binary mixtures are considered, it has been observed that the compounds that show a higher conversion rate when oxidised alone are those whose conversion rate is reduced more significantly in mixture, while the compounds that react more slowly are those with a stronger inhibition effect (Mazzarino and Barresi, 1993).

The same qualitative behaviour occurs in multicomponent mixtures (see Figure 3). Comparing the reaction rates measured in mixture with those of the pure compounds (Fig. 1) it can be observed that the reduction can be very significant; in some cases (e.g. for benzene when styrene is present) it is dramatic. The inhibition effect is strongly influenced by the relative concentration of the hydrocarbons (Barresi *et al.*, 1992). In multicomponent mixtures the relative reactivity of the compounds varies depending on the relative

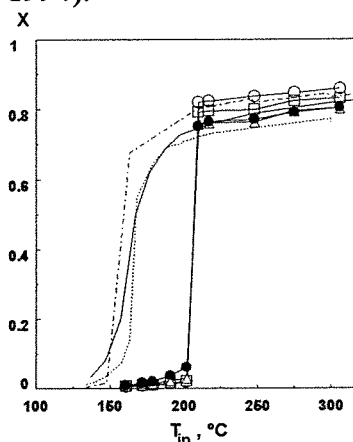


Fig. 4 - Conversion of the individual species vs. inlet temperature for a four-component mixture (about 500 ppmV of each component, in air); symbols as in Fig. 3. Pure benzene conversion is shown for comparison (—, 500 ppmV; ---, 1000 ppmV; - - -, 2000 ppmV). Space velocity = 134,000 h<sup>-1</sup>.

proportional to the maximum specific mass transfer flow. The analysis of the data indicates that, once the heat effects are taken into account, the differences between the regression line for the mixtures benzene-styrene, which show the largest apparent deviations, and that for the other cases are not statistically relevant.

### Dynamic behaviour

Significant stop effects have been observed in the oxidation of the pure compounds and of their mixtures. Some dynamic responses given by toluene in air are shown in Figures 6 and 7, as an example. Similar

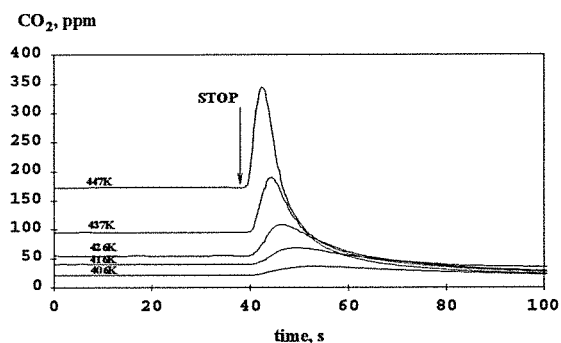


Fig. 6 - Toluene dynamic response at different reaction temperatures; 1000 ppmV in air.

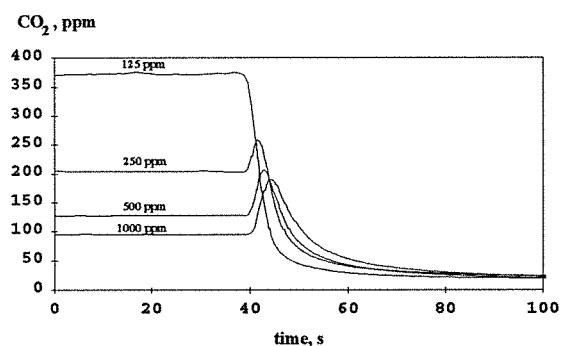


Fig. 7 - Toluene dynamic response at different initial concentrations;  $T = 437\text{ K}$ .

that caused by the end effects of the apparatus; at high concentration the maximum increase in the reaction rate becomes independent of the concentration.

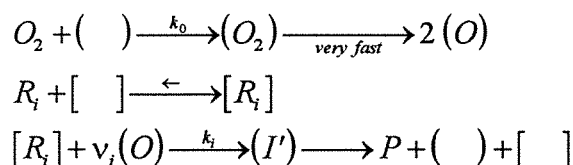
Comparing the stop response curves of different hydrocarbons in the same operative conditions, indications on the relative strength of adsorption can be obtained: these are consistent with that derived from the steady state behaviour of multicomponent mixtures.

Some insight in the dynamics of the elementary reaction steps of the different compounds can be obtained by the analysis of the dynamic response of the binary mixtures: work is currently in progress.

### Kinetic model

A model has been previously proposed elsewhere (Barresi and Baldi, 1994) to describe the steady state behaviour of single compounds and complex mixtures. It can account for apparent zeroth order reaction of single compounds and inhibition effects in mixtures.

It assumes adsorption of oxygen and hydrocarbons over different sites and is schematically shown below, where R stays for the hydrocarbon, P for the products (carbon dioxide and water) and I' for a generic intermediate:



$k_i$  is the kinetic constant of the elementary kinetic step determining the rate of the surface reaction,  $k_0$  the kinetic constant of oxygen chemisorption, ( ) and [ ] the adsorption sites of oxygen and hydrocarbon, respectively.

behaviours have been obtained for benzene and ethylbenzene.

Shortly after stopping the aromatic hydrocarbon feed, a peak in the outlet concentration of  $CO_2$  is observed, which corresponds to a sharp increase in the surface reaction rate. This is consistent with the negative reaction order with respect to the hydrocarbon observed at very low concentration: decreasing the VOC concentration over the catalyst, the concentration of the sites available for oxygen adsorption increase, and a maximum in the reaction rate is observed; of course the role of VOC desorption must also be taken into account.

It can be observed that, in the kinetic control regime, increasing the reaction temperature the peak height increases, while the response time decreases (cf. Fig. 6); at higher temperatures the reaction becomes mass transfer controlled: the conversion rate increases a lot, but no peaks are observed.

The stop effects are also influenced by the initial aromatic concentration, as shown in Figure 7; here, conditions in which the negative reaction order is apparent have been considered. At very low concentration no peak is observed, and the response is

A non-equilibrium adsorption is adopted for oxygen; furthermore the atomic oxygen reacts quickly with the adsorbed hydrocarbon, so that the concentration of (O) on the surface is very low and desorption is negligible. The hydrocarbon is assumed strongly adsorbed on its sites, with a surface coverage close to unity; this explains the apparent zeroth order kinetics observed.

Inhibition is explained by hydrocarbon competition for adsorption on the catalyst.

The rate equation for the  $i$ -component in a general multicomponent mixture is:

$$r_{i_{mix}} = \frac{k_0 k_i p_{O_2}}{k_0 p_{O_2} \left( 1 + \sum_{\substack{j=1 \\ j \neq i}}^n \frac{b_j p_j}{b_i p_i} \right) + v_i k_i + \sum_{\substack{j=1 \\ j \neq i}}^n v_j k_j \frac{b_j p_j}{b_i p_i}}$$

where  $b_i$  and  $p_i$  are the adsorption constant and the partial pressure of the  $i$ -th hydrocarbon.

Fundamental kinetic studies support the proposed model: the adsorption mechanism is the same for the different aromatics, and the relative stability of the adsorbed complexes is consistent with the observed behaviour (Barresi and Baldi, 1994).

For benzene it has been shown that a carbonaceous overlayer is formed over the faces of the platinum crystals, while the edges and the corners, much more reactive, remain clean. Non-dissociative adsorption takes place on low Miller index surfaces below 500 K, while bond breaking occurs on high Miller index planes, that is on stepped surfaces.

The two-adsorption-sites model may thus be justified considering that the catalyst surface is partially covered with a partially dehydrogenated carbonaceous overlayer, from which islands of platinum clusters protrude; these islands are actually atoms in steps and kinks, that are active in bond breaking, and that together with their vicinal sites represent areas of high turnover number and remain clean. Thus, for sake of simplicity, the low Miller planes may be identified with the hydrocarbon adsorption sites, while oxygen adsorbs on stepped surfaces, where the carbonaceous overlayer is continuously oxidised.

The previous model can be easily modified in order to account for the behaviours observed at very low concentration (negative reaction order) and dynamic conditions (stop effect). In fact the assumption of two distinct adsorption sites for oxygen and hydrocarbons derive from the consideration of the heterogeneity of the surface and of the different behaviour of the hydrocarbons over the different sites, and from the assumption that the adsorption of the VOC over the surface is strongly favoured with respect to that of the oxygen. At very low hydrocarbon partial pressure (or if the feed is stopped), sites otherwise occupied by the aromatics become available for oxygen adsorption: as a consequence its surface concentration increases, and the conversion rate can show a maximum. Of course, an additional parameter must be taken into account in the model: the relative concentration of the two energetically different types of adsorption sites.

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## References

- Barresi A., 1990, *Ossidazione catalitica di composti organici volatili presenti nelle emissioni gassose*. Ph.D. Dissertation, Politecnico di Torino, Torino.
- Barresi A.A. and Baldi G., 1992, *Chem. Engng Sci.* **47**, 1943-1953.
- Barresi A.A. and Baldi G., 1994, *Ind. Eng. Chem. Res.* **33**, 2964-2974.
- Barresi A., Mazzarino I. and Ruggeri B., 1989, *Chim. Ind. (Milan)* **71**, 64-75.
- Barresi A.A., Mazzarino I. and Baldi G., 1992, *Can. J. Chem. Eng.* **70**, 286-293.
- Boudart M., 1994, *Ind. Eng. Chem. Res.* **33**, 2900-2903.
- Dumesic J.A., Rudd D.F., Aparicio L.M., Rekoske J.E. and Treviño A.A., 1993, *The microkinetics of heterogeneous catalysis*. ACS, Washington.
- Eigenberger G. and Nieken U., 1994, *Int. Chem. Eng.* **34**, 4-16.
- Matros Yu.Sh., 1985, *Unsteady processes in catalytic reactors*. Elsevier, Amsterdam.
- Mazzarino I. and Barresi A.A., 1993, *Catal. Today* **17**, 335-347.
- Renken A., 1993, *Int. Chem. Eng.* **33**, 61-71.
- Renken A., Doepper R. and Schmid M., 1989, *Dechema-Monogr.* **120**. VCh, Weinheim-New York, 273-290.
- Spivey J.J., 1987, *Ind. Eng. Chem. Res.* **26**, 2165-2180.



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